Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/NL04/000831

International filing date: 01 December 2004 (01.12.2004)

Document type: Certified copy of priority document

Document details: Country/Office: EP
Number: 03078774.1
Filing date: 01 December 2003 (01.12.2003)

Date of receipt at the International Bureau: 11 February 2005 (11.02.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)

Europäisches Patentamt | European Patent Office | Office européen des brevets

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03078774.1

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk

Europäisches Patentamt | European Patent Office | Office européen des brevets

Anmeldung Nr:
Application no.: 03078774.1
Demande no:

Anmeldetag:
Date of filing: 01.12.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Nederlandse Organisatie voor Toegepast-
Natuurwetenschappelijk Onderzoek TNO
Schoemakerstraat 97
2628 VK Delft
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Ecological protected material

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C04B/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

112

Title: Ecological protected material

The invention relates to a material, in particular a natural material provided with a microorganism. The invention further relates to a method of treating material and to the use of such a material.

The protection of materials, in particular biodegradable materials such as wood, is in practice usually accomplished by treating the material with biocidal chemical, in particular fungicidal chemicals. The durability of wood is for instance improved by applying metal salts such a salts of copper, chromium and/or arsenic or by organic biocidal compounds.

From an environmental and health viewpoint, the use of such biocidal compounds is undesired. Accordingly, environmental and health regulations put more and more strict limits on the use of such compounds.

US-A 5 356 624 describes a method for retarding the growth of wood-degrading fungi by treating the wood with an effective amount of a viable, nonsporulating, *Streptomyces rimosus* strain. Grown cells, which produce a metabolite, which stops fungal attack, are used to treat the wood by incubation.

US-A 5 534 252 relates to a method for controlling sapstain in wood, wherein otherwise untreated wood is steam pasteurised and then dipped in a spore solution containing spores of a fungus from the class *Hyphomycetes*.

There remains a continuing need for environmentally friendly materials with a satisfactory resistance against deterioration due to influence of micro- organisms and/or weather-effects, such as UV-radiation and moisture. It has been found that a satisfactory resistance against deterioration due to degrading micro- organisms and/or weather effects such as UV-radiation and moisture is achieved by a material provided with a combination of specific substances and protecting microorganisms.

Accordingly, the present invention relates to a material, comprising a base material provided with a substance which is insoluble in water, a growth substrate and a protecting microorganism layer.

It has been found that a material according to the invention has a very good dimensional stability with a low tendency to formation of cracks.

A material according to the invention has been found to have a very good resistance against degrading microorganisms, such as a rot.

A material according to the invention further has been found to have a durable homogenous surface colour.

A material according to the invention has been found to be very suitable for use as a construction or building material. A material according to the invention has been found very suitable in outdoor applications, such as in garden utilities. In particular, it has been found very suitable as a material, in an application without substantial soil contact. Examples of such applications are garden furniture, fences, façade element and cladding.

Figure 1 shows a possible embodiment of the invention. Herein the base material 4 is subdivided in a non-impregnated core zone 4b and an outer zone 4a, impregnated with water insoluble substance. The hatched area 5 in zone 4a represents the impregnated material present in parts of the material that are penetrated by hyphae of the micro-organisms. Area 5 may be non-impregnated or impregnated to a lesser extent than the surrounding area 5. Of course the impregnation may also be homogenous throughout the zone 4. In this embodiment a water insoluble coating 3 is present at the surface of the base material 4a. On top of the coating 3 a growth substrate layer 2 is present. The micro- organism layer 1 forms the outer surface of the material.

As a base material, any material may be used, in particular material that is susceptible to deterioration by microorganisms. Preferred base materials are wood, concrete, stone and ceramics. Very good results have been achieved with a natural material, in particular with wood, more in particular with softwood (such as pine). The treatment however may be applied for any wood species.

The term "water-insoluble substance" is in general used herein to describe a substance that prevents or at least slows down the penetration of liquid water into the base material.

Very good results have been achieved with a water-insoluble substance comprising at least one organic compound. Such an organic compound is preferably selected from the group consisting of mineral oils, waxes, vegetable- and animal oils, including mixtures and water-insoluble derivatives of any of these compounds.

In particular a C4 to C32 saturated or unsaturated fatty acid ester of a fatty acid with a polyol, such as glycerol, has been found very suitable.

Good results have *inter alia* been achieved with an oil extracted from a seed or fruit. Examples of such oils are film forming vegetable oils. Very good results have been achieved with linseed oil and with hempseed oil.

Optionally, the water-insoluble substance is present in a mixture with one or more other additives, such as one or more additives selected from the group consisting of amino acids and pentosans. These additives can be used as nutrients by the microorganisms. Additives from the group of metal-salts may be used in order to improve polymerisation of the substrate, which may have a positive effect on the durability of the wood.

A preferred material according to the invention comprises a water-insoluble coating 3 on top of the surface of the base material 4. The presence of such a coating has been found to have very good blocking properties against penetration of water. Further, it is thought that such a coating contributes to levelling the surface of the base material, which may contribute to a favourable uniform microorganism layer. In addition, the presence of a water-insoluble coating has been found to cooperate with the protective microorganism layer to shield the base material against degrading microorganisms.

Advantageously, water insoluble coating has a thickness in the range of about 1-1000 μm. Such a layer thickness has been found to contribute

to a desired evenness of the protective microorganism layer Very good results have been achieved with a thickness of at least 5 μm.

The material may be partially or fully impregnated or coated with the water-insoluble substance.

The growth substrate may be present in the microorganism layer, in a mixture with the water-insoluble substance and/or as an intermediate growth substrate layer between the microorganism layer and the base material.

Organic substances produced from vegetable or animal resources can be used as nutrients for the growth of the microorganisms. As a growth medium, preferably a substrate based on digestible carbohydrates is used.

The microorganism or organisms are preferably chosen in order to fulfil the requirements related to the use such as UV-resistance, tolerance to climatic and weather changes (temperature and moisture availability). It is further desirable that the microorganisms do not degrade the base material but form a protecting layer. It is preferred that the functional properties and appearance of the system can be controlled by use of adequate organisms, additives, composition of various parts of the system or variations in the production process.

Preferred are microorganisms which grow on surfaces of materials under extreme climate conditions but are not (severely) damaged by extreme climate conditions. Suitable are for instance microorganisms from the group of fungi, bacteria and yeasts. Preferred microorganisms include microorganisms from the group of black yeasts and related fungi.

For instance, use may be made of a microorganism comprising a pigmentation system (hereafter referred to as pigmented microorganism), such as *Aureobasidium spp.*, which has been found suitable to influence a surface appearance like gloss, colour or opacity.

The range of the colours may be found in the whole visible spectrum, the gloss may be in the range of 0-80% (intensity, reflection of scattered light according to ISO 2814).

The microorganism layer preferably fully covers the base material.

The microorganism layer preferably is the outermost layer of the material and/or has grown through the substrate.

The microorganism layer may be a single layer of microorganism cells. The thickness of the microorganism layer is preferably less than 1 000 μm, more in particular between about 1 and about 100 μm. More preferably the thickness of the microorganism layer is at least 5 μm.

The microorganism layer preferably essentially consists of microorganisms and one or more nutrients which can be originating from the growth substrate or precipitated from the surrounding environment.

The microorganism layer may contribute to the visual appreciation of the product, in particular when a (strongly) coloured microorganism is present such as *Aureobasidium spp.* Such a microorganism may provide a uniform and reproducible colour varying from light colours (red, green) to almost black) throughout the surface of the material.

Besides using the microorganism in order to give the material a homogeneous appearance, it has been found that a pigmented microorganism contributes to the resistance of the base material against deterioration due to UV-radiation.

Besides having good protective properties, it has been found that such a layer contributes to a durable optical quality of the surface. Indicative rubbing tests showed that that the mechanical resistance is satisfactory.

The invention further relates to a method for preparing a material such as a material according to the invention, comprising providing a base material with a hydrophobic substance, a growth substrate and a microorganism layer.

More in particular a method according to the invention comprises

- applying a water insoluble substance to the base material;
- applying a growth substrate to the base material together with the water insoluble substance and/or after applying the water insoluble substance; and
- covering the base material comprising the water insoluble substance with a microorganism layer, which layer optionally comprises growth substrate.

Preferably, the base material is initially subjected to application of the water-insoluble substance and the growth substrate provided with the microorganisms. This treatment is believed to contribute to the protection of the material against degrading microorganisms.

Depending upon the type of material, the treatment conditions, such as temperature, pressure, duration and atmosphere may suitably be chosen based upon common general knowledge and the information disclosed in the present claims and description, including the cited references.

In general, during the treatment the temperature of the medium surrounding the material may be kept in the range between 20°C and 240°C for a period of time. The upper limit of the temperature is in practice determined by the material properties. In general, a treatment at a temperature in the range of 60-140 °C, in particular in the range of 70-120°C has been found to be effective, especially when treating wood.

The duration of the treatment *inter alia* depends on the geometry of the material, and the desired substrate uptake. In general, it is preferred that the treatment is carried out for a duration that is sufficient to heat up the material or part of the material to a temperature of about 60 °C or more. Good results have *inter alia* been achieved with a treatment in the heated medium of at least about 2 minutes, preferably of at least about 1 hour. A treatment of up to about 2 hours is in general satisfactory.

The application of the growth substrate together with the microorganisms may suitably be carried out in a process described in IRG/WP 97-20113 (1997) or a normal coating process.

The invention further relates to a material obtainable by a method according to any one of the claims.

The invention is further illustrated by the following example:

Example 1

Table 1: Example of this treatment after 3 years exposition

Material	Mass change after 3 years exposition	Remarks
Untreated pine sapwood (Control)	-5 %	Degradation confirmed by microscopic assessment
pine sapwood, subjected to treatment I (invention)	0.0 %	No degradation noticed
pine sap wood, subjected to treatment II (invention)	0.0 %	No degradation noticed
Reference Example (pine sapwood with Cu-HDO (Copper-cyclohexyldioxydieazeniumoxide)	-1.2%	No degradation, mass change probably caused by leaching

Treatment I involved an impregnation of the wood in an standard impregnation kettle. The wood was placed in the kettle in a bath of 75 % linseed oil in a solvent (*e.g.* acetone). While the wood was in the bath first a vacuum ($8x10^3$ Pa) was applied for 0.2 hr.. Next, the impregnation was pressurised for 1.5 hr. at $8x10^5$ Pa to allow impregnation of the oil into the wood. Thereafter the wood was taken out of the kettle and placed in an oven, heated at 103 °C for 96 hr. The temperature in the core of the wood reached 100 °C.

In treatment II hempseed oil was used instead of linseed. The other conditions were the same as in treatment I.

Claims

1. Material, comprising a base material (4) provided with a water-insoluble substance, a growth substrate and a covering microorganism layer.

2. Material according to claim 1, wherein the water-insoluble substance is present in a coating (3) on top of the surface of the base material.

3. Material according to claim 1 or 2, wherein the water insoluble coating has a thickness in the range of 1-1000 μm.

4. Material according to any one of the preceding claims, which is at least partially impregnated with the water-insoluble substance.

5. Material according to any one of the preceding claims, wherein the water-insoluble substance is a mineral oil or wax, a vegetable oil or wax or an animal oil or wax, preferably a vegetable oil or vegetable wax.

6. Material according to claim 5, wherein the water-insoluble substance is selected from the group C4 to C32 saturated and unsaturated fatty acid-esters, and preferably is a fatty acid ester of a fatty acid with glycerol or another polyol.

7. Material according to any one of the preceding claims, wherein the growth substrate is present in the microorganism layer (1), and/or as an intermediate growth substrate layer (2) between the microorganism layer (1) and the base material (4), preferably adjacent to the microorganism layer.

8. Material according to any one of the preceding claims, wherein the growth substrate layer has a thickness between 0 and 1000 μm.

9. Material according to any one of the preceding claims, wherein the growth substrate comprises at least one substance selected from the group consisting of carbohydrates and proteins including derivates and mixtures thereof.

10. Material according to any one of the preceding claims, wherein the thickness of the microorganism layer is less than about 1000 µm, preferably from about 5-100 µm.

11. Material according to any one of the preceding claims, wherein the microorganism comprises at least one microorganism selected from the group consisting of bacteria and fungi - preferably from the group of black yeasts and related fungi.

12. Material according to any one of the preceding claims, wherein the base material is a natural material.

13. Material according to any one of the preceding claims, wherein the base material is selected from the group consisting of wood, concrete, ceramic and stone, preferably wood based products.

14. Material according to any one of the preceding claims wherein the material is a construction or building material.

15. Method for preparing a material according to any one of the preceding claims, comprising providing a base material with a water-insoluble substance, a growth substrate and a microorganism layer.

16. Method according to claim 15, wherein the water-insoluble substance is applied, then a growth substrate layer and thereafter the water-insoluble substance with a microorganism layer.

17. Method according to claim 15 or 16, wherein the base material is subjected to a treatment in a heated medium while applying the water-insoluble substance.

18. Method according to any one of the claims 15-17, wherein the base material is subjected to a treatment at a temperature in the range of 20-240 °C, preferably of 70-120 °C.

19. Method according to any one of the claims 15-18, wherein the microorganisms are incorporated in the water-insoluble substance.

20. Use of a material according to any one of the claims 1 to 14 in an application without soil contact.

21. Garden furniture, fence, façade element or cladding comprising a material according to any one of the claims 1-14.

Title: Ecological protected material

Abstract

The present invention relates to an ecological protected material, comprising a base material (4) provided with a water-insoluble substance, a growth substrate and a microorganism layer. The invention further relates to a method for preparing a material according to the invention, comprising providing a base material with a water-insoluble substance, a growth substrate and a microorganism.

FIGURE 1